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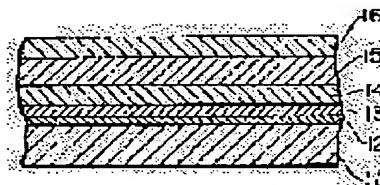
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(54) PIEZO-ELECTRIC THIN FILM ELEMENT, AND ACTUATOR AND INK-JET TYPE RECORDING HEAD USING THE THIN FILM ELEMENT AND MANUFACTURE OF PIEZO-ELECTRIC THIN FILM ELEMENT

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the reduction of the oxygen concentration in a piezo-electric thin film and to improve the characteristics of a piezo-electric body in the process for forming the piezo-electric thin film element by performing heat treatment after the formation of a lower electrode and before the formation of the piezo-electric thin film under oxygen atmosphere.

SOLUTION: A piezo-electric thin film element has a silicon substrate 11, a silicon oxide film 12 formed on the substrate 11, a titanium film 13 formed on the oxide film 12, a titanite-acid lead zirconate (PTZ) film 15 of the piezo-electric thin film formed on a lower electrode 14 and an upper electrode 16 formed on the film 15. Before the PTZ is annealed, the heat treatment of the lower electrode 14 is performed under the presence of oxygen. Thus, the oxygen in the piezo-electric thin film 15 is trapped in each grain boundary in the lower electrode 14. By the heat treatment of the lower electrode 14 under the oxygen atmosphere, the compound of the oxygen diffused into platinum and Ti appears as round particles equally dispersed in the lower electrode 14. Therefore, the piezo-electric thin film 15 having the excellent characteristics of the piezo-electric body is obtained by preventing the reduction of the oxygen concentration in the piezo-electric thin film 15.



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the piezo electric crystal thin film characterized by forming a top electrode and a bottom electrode on both sides of the piezo electric crystal film, and heat-treating under an oxygen ambient atmosphere in the manufacture approach of the piezo electric crystal thin film which carries out the formation postheat treatment of said piezo electric crystal on a bottom [this] electrode before after [said bottom electrode formation] piezo electric crystal thin film formation.

[Claim 2] The approach according to claim 1 said oxygen ambient atmosphere is 60% or more of oxygen tension.

[Claim 3] The piezo electric crystal thin film which comes to heat-treat said bottom electrode under oxygen existence in the piezo electric crystal thin film equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode before forming a piezo electric crystal thin film on said bottom electrode.

[Claim 4] The piezo electric crystal thin film characterized by the oxygen ratio of concentration (r) of the oxygen density of the piezo electric crystal near said bottom electrode and a piezo electric crystal thin film being in or more 0.9 1.2 or less range in the piezo electric crystal thin film equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode.
 $r = (\text{oxygen density in the piezo electric crystal film the oxygen density} / \text{near the bottom electrode})$ [in a piezo electric crystal thin film]

[Claim 5] The actuator which uses said piezo electric crystal thin film according to claim 3 or 4 as a mechanical stress generating means.

[Claim 6] The ink jet type recording head equipped with said actuator according to claim 5.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of a piezo electric crystal thin film. Furthermore, this invention relates to the piezo electric crystal thin film obtained using this manufacture approach, and the actuator using this.

[0002]

[Description of the Prior Art] This actuator transforms electric energy into mechanical energy, or performs that reverse, and is used for a pressure sensor, a temperature sensor, an ink jet type recording head, etc. In the ink jet type recording head, the piezo electric crystal thin film is used as vibrator used as the driving source of the ink regurgitation.

[0003] This piezo electric crystal thin film has the structure generally equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode. Generally the presentation of this piezo electric crystal thin film is made into the binary system which uses titanite-acid lead zirconate (henceforth "PZT") as a principal component, or the three-component system which added the third component to PZT of this binary system.

[0004] The piezo electric crystal thin film of these presentations can be formed with a sputter, a sol gel process, the laser ablation method, or a CVD method.

[0005] The ferroelectric using binary system PZT as these examples is indicated by "Applied Physics Letters, 1991, Vol.58, No.11, and pages 1161-1163." Moreover, JP,6-40035,A and the piezo electric crystal which used binary system PZT for "Journal of The American Ceramic Society, 1973, Vol.56, No.2, and pages 91-96" are indicated.

[0006] When applying said piezo electric crystal thin film to for example, an ink jet type recording head, a piezo electric crystal thin film (PZT film) equipped with 0.4 micrometers - about 20 micrometers thickness is desired. Furthermore, since a high piezoelectric strain constant is required of this piezo electric crystal thin film, it heat-treats at the temperature of 700 degrees C or more, and it is usually supposed that it is required to grow up the crystal grain of this piezo electric crystal thin film.

[0007]

[Problem(s) to be Solved by the Invention] However, this invention person came to acquire the knowledge of the oxygen density in a piezo electric crystal thin film falling, and degrading a piezoelectric strain constant by this heat treatment. Then, the following judgments were acquired when this invention person examined this reason wholeheartedly. That is, the platinum used as the bottom electrode of a piezo electric crystal thin film is rich in the property to adsorb oxygen so that clearly from it being what is used as an oxidation catalyst.

[0008] Therefore, a bottom electrode is made combined with the titanium which carried out the trap of the oxygen in PZT when PZT was sintered, and has been diffused in a bottom electrode.

[0009] Then, this invention aims at offering the manufacture approach of a piezo electric crystal thin film excellent in the piezo electric crystal property in the process which forms a piezo electric crystal thin film by preventing lowering of the oxygen density in a piezo electric crystal thin film, in order to solve such a technical problem.

[0010] Other objects of this invention are offering such a piezo electric crystal thin film. The object of further others of this invention is offering the actuator equipped with this piezo electric crystal thin film, especially an ink jet type recording head.

[0011]

[Means for Solving the Problem] In order to attain this object, this invention forms a top electrode and a bottom electrode on both sides of the piezo electric crystal film which consists of the polycrystalline substance, and is characterized by heat-treating under an oxygen ambient atmosphere before after [said bottom electrode formation] piezo electric crystal thin film formation in the manufacture approach of the piezo electric crystal thin film which carries out the formation postheat treatment of said piezo electric crystal on a bottom [this] electrode. Said oxygen ambient atmosphere is desirable and oxygen tension is 60% or more of range (with volume ratio). When oxygen tension is less than 100%, other gas is nitrogen or an argon.

[0012] Furthermore, in the piezo electric crystal thin film equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode, before the piezo electric crystal thin film concerning this invention forms a piezo electric crystal thin film on said bottom electrode, it heat-treats and said bottom electrode consists of under oxygen existence.

[0013] Moreover, other piezo electric crystal thin films concerning this invention are characterized by the oxygen ratio of concentration (r) of the oxygen density in the piezo electric crystal thin film near said bottom electrode and a piezo electric crystal thin film being in or more 0.9 1.2 or less range in the piezo electric crystal thin-film thing equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode. Here, an oxygen density (r) is displayed as follows. Near means less than $10 \times 10^{-9} \text{m}$.

[0014] $r = (\text{oxygen density in the piezo electric crystal film} / \text{near the bottom electrode})$ [in a piezo electric crystal thin film]

Furthermore, this invention is characterized by being the actuator which uses said piezo electric crystal thin film as a mechanical stress generating means. Furthermore, this invention is characterized by being the ink jet type recording head equipped with said actuator.

[0015]

[Embodiment of the Invention] Next, the gestalt of operation concerning this invention is explained with reference to a drawing. In addition, the gestalt of this operation explains the case where the PZT film is formed as piezo electric crystal film.

[0016] (Gestalt 1 of operation) Drawing 1 is the sectional view showing the configuration of the piezo electric crystal component concerning this invention. This piezo electric crystal thin film is equipped with the electrode 16 after being formed on a silicon substrate 11, the silicon oxide 12 formed on the silicon substrate 11, the PZT film 15 formed on silicon oxide the titanium film (Ti/TiO₂/Ti) 13 formed 12 top and the bottom electrode (Ti/Pt) 14, and the PZT film 15, and is constituted.

[0017] Said bottom electrode 14 is formed from the platinum combined with the layer of titanium and titanium oxide like previous statement at the time of film production. By making the bottom electrode 14 such a configuration, since it says that the lattice constant of the bottom electrode 14 and the lattice constant of the PZT film 15 can carry out near, adhesion with the PZT film 15 formed in behind can be raised.

[0018] The titanium layer which consists of (Ti/TiO₂/Ti) is formed for raising the adhesion between silicon oxide and a platinum layer on silicon oxide 12. Furthermore, Ti is formed on platinum for making a piezo-electric thin film into a columnar structure like the after-mentioned.

[0019] this invention persons have proposed from sometime past that a piezo electric crystal property can be improved by making the crystal structure of a piezo electric crystal thin film into a columnar structure. The crystal structure of a piezo electric crystal thin film can be adjusted to structure which raises a piezo electric crystal property by forming titanium in the shape of an island on platinum.

[0020] In addition, (Ti/TiO₂/Ti) of the titanium film is not observed with a scanning electron microscope by annealing performed after PZT film production as what is spread in Pt or SiO₂ and

forms a layer special on a bottom electrode, either.

[0021] The PZT film 15 consists of the polycrystalline substance, and the grain boundary of this crystalline exists in the abbreviation perpendicular direction to the flat surface of the vertical electrodes 14 and 16, as shown in drawing 3 and drawing 4. That is, the crystal grain of PZT has accomplished the columnar structure.

[0022] That to which this PZT film 15 uses binary system as a principal component, and the thing which uses as a principal component three-component system which added the third component to this binary system are used suitably. What has the presentation expressed with the chemical formula of $Pb(Zr_xTi_{1-x})O_3 + YPbO$ (being here $0.40 \leq x \leq 0.6$, $0 \leq Y \leq 0.3$) as a desirable example of binary system PZT is mentioned.

[0023] Moreover, as a desirable example of three-component system PZT, what has the presentation expressed with the chemical formula shown in the following which added the third component is mentioned to PZT of said binary system.

[0024]

$PbTi_aZr_b(AgBh)_cO_3 + ePbO + (fMgO)_n$ (here, A expresses the trivalent metal chosen from the group which consists of a divalent metal chosen from the group which consists of Mg, Co, Zn, Cd, Mn, and nickel, or Sb, Y, Fe, Sc, Yb, Lu, In and Cr.) Moreover, B expresses the pentavalent metal chosen from the group which consists of Nb, Ta, and Sb, or the metal of 6 ** chosen from the group which consists of W and Te. Moreover, although it is $a+b+c=1$, $0.35 \leq a \leq 0.55$, $0.25 \leq b \leq 0.55$, $0.1 \leq c \leq 0.4$, $0 \leq e \leq 0.3$, $0 \leq f \leq 0.15$, $g=f=1/2$, and $n=0$ however, A — a trivalent metal — it is — and B — the metal of 6 ** — not but — moreover, the case where g is 1/3, and h is 2/3, and Mg and B of A are Nb(s) when A is a divalent metal and B is a pentavalent metal — as long as — n expresses 1.

As a more desirable example of three-component system, magnesium lead niobate, i.e., A, is Mg, B is Nb, and that 1/whose 3h g is 2/3 is mentioned.

[0025] Furthermore, even if it is any of these binary system PZT and three-component system PZT, in order to improve the piezo-electric property, Ba, Sr, La, Nd, Nb, Ta, Sb, Bi, W, Mo, calcium, etc. of a minute amount may be added. In three-component system, addition of Sr not more than 0.10 mol % and Ba is especially much more desirable to an improvement of a piezo-electric property. Moreover, since addition of Mn not more than 0.10 mol % and nickel improves the degree of sintering in three-component system, it is desirable.

[0026] In the process which forms the piezo electric crystal thin film 15, in order to acquire structure like previous statement, predetermined heat treatment is performed. According to the place which this invention persons examined, the oxygen in PZT is spread in a bottom electrode in the case of this heat treatment. If a bottom electrode is formed by sputtering so that it may mention later, it will check that an electrode has a columnar structure like PZT. In this crystal structure, the inclination for the trap of the oxygen to be carried out to a grain boundary is strong, and the titanium diffused in platinum forms an oxide in this grain boundary.

[0027] Then, this invention person proposed forming heat treatment for a bottom electrode under oxygen existence, before annealing PZT, as shown below. Drawing 4 is the scanning microphotography which shows the cross section of the cross direction of the piezo electric crystal thin film formed by the approach described below, and was obtained under conditions with an acceleration voltage [of 15kV], and a cash-drawer electrical potential difference of 4.0kV.

[0028] According to this, it turns out that a bottom electrode and the piezo electric crystal film have the pillar-shaped crystal structure mostly mentioned already. The trap of the oxygen in a piezo electric crystal thin film is carried out to each grain boundary in a bottom electrode. Moreover, it has appeared as a round grain which the compound of the oxygen and Ti which were diffused in platinum is among a bottom electrode, and carried out division-into-equal-parts powder by heat treatment under the oxygen ambient atmosphere of a bottom electrode.

[0029] Next, the manufacture approach of the piezo electric crystal thin film concerning 1 operation gestalt of this invention is explained with reference to a drawing.

[0030] Drawing 5 (a) thru/or drawing 5 (c) are the sectional views showing the production process of the piezo electric crystal thin film mentioned above. At the process shown in drawing 5 (a), it oxidizes thermally to a silicon substrate 11, and the silicon oxide 12 whose thickness is about 0.3-

1.2 micrometers is formed on a silicon substrate 11. Next, the thickness as the whole forms the titanium film 13 which consists of Ti/TiO₂/Ti (0.01 micrometers thru/or about 0.04 micrometers) on silicon oxide 12 by the sputter. Subsequently, the bottom electrode 14 which consists of platinum is formed by about 0.2–0.8–micrometer thickness on the titanium film 13 by the sputter. [0031] The sputter conditions at this time are as follows. The direct-current sputtering system was used as equipment. A sputter flow and pressure requirement is 0.4Pa. In Pt, electrical-potential-difference conditions are 1kw(s), and, in the case of Ti, it is 200w, and, in TiO₂, is 300w. In the case of Pt and Ti, the conditions of a controlled atmosphere are among an argon, and, in TiO₂, it is O₂/Ar=10/90.

[0032] subsequently, the component in the middle of this film production — a diffusion furnace — putting in — the bottom of an oxygen ambient atmosphere (60% or more of oxygen tension), 400, or 600 degrees C — 30 — or it heats for 60 minutes. or a RTA (Rapid Thermal Annealing) furnace — this component — putting in — the inside of an oxygen ambient atmosphere (flow rate 5 L/min) — temperature 400 thru/or 600 degrees C — time amount — 60 — or it heats for 300 seconds.

[0033] Next, titanium is formed in the shape of an island by the sputter on the bottom electrode 14 formed at the process shown in drawing 5 (a) like the process shown in drawing 5 (b). Orientation of the crystal structure of a piezo electric crystal thin film can be strongly carried out to the 100th page by making this titanium into 40 thru/or 60A thickness.

[0034] Subsequently, this PZT film 15 is produced on this. This is performed with a sol gel process. Here, suppose that PZT is manufactured with the multilayer coat of two coats 8 times using a sol gel process. This sol gel process is as follows.

[0035] This manufacture approach is an approach of carrying out dehydration processing of the hydration complex of the hydroxide of the metal component which can form the PZT film 15, i.e., the sol, considering as gel, carrying out heating baking of this gel, and adjusting an inorganic oxide. This manufacture approach consists of each following process.

[0036] a. In the gestalt of membrane formation process book operation of a sol constituent, the sol of the metal component which constitutes the PZT film can hydrolyze and adjust from an acid the metaled alkoxide or the acetate which can form the PZT film. In this invention, the presentation of the PZT film mentioned above can be acquired by controlling the presentation of the metal in a sol. That is, let titanium, a zirconium, lead, each alkoxide of the metal component of further others, or acetate be a start raw material.

[0037] Here, there is an advantage that the presentation of the metal component which will constitute the PZT film by the time it considers as the PZT film (piezo electric crystal thin film) eventually is maintained mostly. That is, the presentation of a metal component [in / there are very little metal component and fluctuation especially according to evaporation of a lead component etc. during baking and annealing treatment, therefore / these start raw materials] will be in agreement with the metal presentation in the PZT film obtained eventually. That is, the presentation of gel is determined according to the piezo electric crystal film (the gestalt of this operation PZT film) which it is going to generate.

[0038] Moreover, in order to obtain the PZT film with which the lead component mentioned above becomes superfluous with the gestalt of this operation, 15–mol the thing carried out to an excess to % is preferably more desirable than the amount of which a lead component is required from a stoichiometry in a sol to 20–mol %.

[0039] As for this sol, with the gestalt of this operation, it is desirable to be used as a constituent mixed with the organic high molecular compound. This organic high molecular compound prevents effectively that absorb the residual stress of a thin film at the time of desiccation and baking, and a crack arises in this thin film. If the gel containing this organic macromolecule is specifically used, pore will arise in the gelled thin film which is mentioned later. It is thought that this pore absorbs the residual stress of a thin film in pre annealing and the annealing process which are mentioned further later. Here, as an organic high molecular compound used preferably, polyvinyl acetate, hydroxypropylcellulose, a polyethylene glycol, the polyethylene–glycol monomethyl ether, a polypropylene glycol, polyvinyl alcohol, polyacrylic acid, a polyamide, the poly AMIKU acid, an acetyl cellulose, its derivative, and those copolymers are mentioned.

[0040] In addition, with the gestalt of this operation, the porosity gel thin film which is 1

micrometer or less in magnitude, and had large distribution can be formed by adding hydroxypropylcellulose for the porosity gel thin film which has much about 0.05-micrometer pores by adding polyvinyl acetate.

[0041] With the gestalt of this operation, a with an average molecular weight of about 285 to 420 thing is suitably used as a polyethylene glycol. Moreover, as a polypropylene glycol, a with an average molecular weight of about 300 to 800 thing is used suitably.

[0042] By the manufacture approach concerning the gestalt of this operation, this sol constituent is first applied on the bottom electrode 14 (refer to drawing 5 (b)) which is going to form the PZT film 15. Especially the method of application at this time is not limited, but the approach usually performed, for example, a spin coat, a DIP coat, a roll coat, a bar coat, etc. can perform it. Moreover, it can also apply by flexographic printing, screen-stencil, offset printing, etc.

[0043] Moreover, when the process after it is taken into consideration, as for the thickness of the film formed of said spreading, it is desirable to control so that the thickness of the porosity gel thin film formed in the gelation process mentioned later is set to 0.3 micrometers or less, and it is good to be more preferably referred to as about 0.2 micrometers.

[0044] Next, the applied sol constituent is heated at air drying or the temperature of 200 degrees C or less. Here, said sol constituent can be further applied on this film dried (heating), and thickness can also be thickened. In this case, as for the film used as a substrate, it is desirable to dry at the temperature of 80 degrees C or more.

[0045] b. Calcinate the film obtained at the gelation process of the film which consists of a sol constituent, next the membrane formation process of a sol constituent mentioned above, and form the porosity gel thin film which consists of an amorphous metallic oxide which does not contain the residual organic substance substantially.

[0046] Baking is sufficient temperature to gel the film of a sol constituent and remove the organic substance out of the film, and is performed by [sufficient] carrying out time amount heating. It is desirable to make burning temperature into 300–450 degrees C with the gestalt of this operation, and it is still more desirable to make it 350–400 degrees C.

[0047] Although it changes with temperature and the formats of a furnace to be used, when a cleaning furnace is used for example, about 10 – 120 minutes of firing time are desirable, and it is more desirable to consider as about 15 – 60 minutes. Moreover, when a hot plate is used, about 1 – 60 minutes is desirable, and it is still more desirable to consider as about 5 – 30 minutes.

[0048] Of the above process, the porosity gel thin film was formed on the bottom electrode 14.

[0049] c. Carry out heating baking of the porosity gel thin film obtained at the pre annealing process, next the process b mentioned above, and change this film into the film which consists of a metal oxide film of a crystalline substance.

[0050] What is necessary is not to perform baking until a perovskite mold crystal occupies most during a crystal, and just to terminate it, when a gel thin film crystallizes to homogeneity although carried out at temperature required in order to change a porosity gel thin film into the film which consists of a metallic oxide of a crystalline substance. With the gestalt of this operation, as a burning temperature, the range of 400–800 degrees C is desirable, and it is more desirable to calcinate in the range which is 550–750 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when using an annealing furnace, for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA (Rapid Thermal Annealing) furnace is used, about 0.1 – 10 minutes is desirable, and about 1 – 5 minutes is more desirable.

[0051] Moreover, with the gestalt of this operation, this pre annealing process can be divided into two steps, and can be carried out. As a first stage story, annealing can be performed at the temperature of the range of 400–600 degrees C, next, specifically, annealing can be first performed at the temperature of the range of 600–800 degrees C as a second stage story. Furthermore, as a first stage story, annealing can be performed at the temperature of the range of 450–550 degrees C, next annealing can be preferably performed at the temperature of the range of 600–750 degrees C as a second stage story.

[0052] According to this process, the porosity gel thin film was transformed to the film which consists of a metal oxide film of a crystalline substance.

[0053] d. It consists of a metal oxide film according to the pre annealing process of Process C, and carry out film conversion, after repeating the processes a and b mentioned above further 3 times a repeat process, next henceforth and carrying out the four-layer laminating of the porosity gel thin film. Subsequently, island-like titanium is formed in the shape of an island by the approach as stated above on PZT, and the processes a and b as stated above are repeated further 4 times.

[0054] What is necessary is just to determine suitably the number of laminatings of the cascade screen obtained as a result of this repeat process in consideration of the thickness of the final PZT film 15. Here, it is good that it is 0.15 micrometers of hits much more. In addition, it cannot be overemphasized that it is desirable that it is the thickness which a crack etc. does not generate in degree process (process e) mentioned later.

[0055] At this repeat process, the porosity gel thin film which newly formed the porosity gel thin film and was newly formed on the film formed previously as a result of subsequent pre annealing turns into film formed previously and film unified substantially.

[0056] Here, a discontinuity layer may be not only when there is no discontinuity layer between the layers by which the laminating was carried out to the film unified substantially but between the layers by which the laminating was carried out unlike the case of the PZT film 15 concerning the gestalt of this operation obtained eventually. And in repeating Processes a, b, and c further, a still newer porosity gel thin film is formed, and this new porosity gel thin film turns into film substantially united with the cascade screen of the crystalline substance obtained above as a result of subsequent pre annealing.

[0057] e. Perform annealing on the film obtained at the perovskite mold crystal growth process, next said process d in 800–1000 degrees C still more preferably the burning temperature of 600–1200 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when an annealing furnace is used for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA furnace is used, about 0.1 – 10 minutes is desirable, and about 0.5 – 3 minutes is more desirable.

[0058] Moreover, with the gestalt of this operation, this perovskite mold crystal growth process, i.e., annealing, is divided into two steps, it is carried out, and is made. Annealing is performed at the temperature of about 600–800 degrees C, and, specifically, the temperature of 800–1000 degrees C performs annealing on a second stage story on a first stage story. Furthermore, preferably, annealing can be performed at the temperature of about 600–750 degrees C, and the temperature of 800–950 degrees C can perform annealing on a second stage story on a first stage story.

[0059] Of the above actuation, PZT whose thickness which consists titanium of the polycrystalline substance of the shape of a column which grew as a nucleus is 1.2 micrometers is formed on the bottom electrode 14.

[0060] Next, it precedes forming the piezo electric crystal thin film after bottom electrode formation, and the comparison of a piezo-electric property with the case (comparison method) where it is made the same conditions is shown [all of the case (this invention method) where previous statement is heat-treated, and except for having not performed it].

[0061]

	圧電定数 d_{31}	出力係数 g_{31}	誘電率
本発明法	150 (pC/N)	11.2	1500
従来法	120 (pC/N)	9.0	1500

Thus, according to this invention method, the piezo electric crystal thin film which excelled [all] in the piezo-electric property as compared with the conventional method can be obtained. When this invention person measured the oxygen density in a piezo electric crystal thin film, and the oxygen density in the piezo electric crystal film near 10nm near the bottom electrode in the piezo electric crystal thin film obtained by this invention method, the oxygen density in the piezo electric crystal film near the bottom electrode was large as compared with it in a piezo electric crystal thin film, and it checked that said ratio (r) had been 0.95. Moreover, the oxygen density in the piezo electric crystal film near the bottom electrode was 35 atoms %.

[0062] When this invention person inquires wholeheartedly, as for the ratio (r) of both oxygen

density, it is desirable that it is the range of 0.9 thru/or 1.2, and, as for the oxygen density of the inside near the bottom electrode, it is desirable that it is the range of 30 thru/or 60 atom %. On the other hand, a ratio (r) is about 0.67 and, as for these properties of a conventional method, unlike this invention, lowering of the oxygen density in the PZT film was observed notably. In addition, measurement of these oxygen densities was performed as follows.

[0063] The thin film fragmentation of the piezo electric crystal thin film was carried out with the low angle ion milling system, and the component analysis of this was carried out in TEM (transmission electron microscope). the used equipment and low angle ion milling — Japan Fiji tech and — Hang lei It is made in Linda and TEM is Philip FEG-CM200TEM. In addition, the applied voltage in the case of the XEDX observation by TEM is 200kV.

[0064] A measurement result is data which took the average of four points, and is as follows.

[0065]

	PZT膜中	下電極近傍
本発明	33.8	35.3
従来	26.4	39.2

(The unit of data is atomic %.)

According to this invention, a piezoelectric constant (d31) can be improved 20 to 30% compared with the conventional thing.

[0066] The process of drawing 5 (b) is ended by the above, and it shifts to the process shown in drawing 5 (c) below. At this process, thickness forms the electrode 16 when consisting of about 0.2–1.0–micrometer aluminum by the spatter on the PZT film 15 obtained at the process shown in drawing 5 (b).

[0067] Thus, the piezo electric crystal thin film as shown in drawing 2 was obtained. In addition, it was checked that there is no generating of a crack in the obtained PZT film 15, and the surface of discontinuity of the shape of a layer by the laminating does not exist in a cross section, either.

[0068] Drawing 6 is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[0069] The ink jet type recording head concerning the gestalt 3 of operation The silicon substrate 21 in which the ink reservoir 27 was formed as shown in drawing 6 , The diaphragm 22 formed on the silicon substrate 21, and the bottom electrode 23 formed in the request location on a diaphragm 22, It is on the bottom electrode 23, and it has the piezo electric crystal thin film 24 formed in the location corresponding to the ink reservoir 27, the electrode 25 after being formed on the piezo electric crystal thin film 24, and the 2nd substrate 26 joined to the underside of a silicon substrate 21, and is constituted.

[0070] The bottom electrode 23 has the same configuration as the bottom electrode explained with the gestalt 2 of operation. Moreover, the piezo electric crystal thin film 24 has the same configuration as the PZT film explained with the gestalt 1 of operation.

[0071] Ink is supplied to the ink reservoir 27 through the ink passage which does not illustrate this ink jet type recording head. Here, if an electrical potential difference is impressed to the piezo electric crystal film 24 through the bottom electrode 23 and the top electrode 25, the piezo electric crystal film 24 will deform and a pressure will be applied to the ink in the ink reservoir 27. It is breathed out by this pressure from the nozzle which ink does not illustrate, and ink jet record is performed with it.

[0072] Since the piezo electric crystal thin film excellent in the piezo–electric property as stated above is used for this ink jet type recording head as vibrator, it can make ink breathe out by the big pressure here.

[0073]

[Effect of the Invention] As explained above, according to the manufacture approach of the piezo electric crystal thin film concerning this invention, in the process which forms a piezo electric crystal thin film, the piezo electric crystal thin film excellent in the piezo electric crystal property can be offered by preventing lowering of the oxygen density in a piezo electric crystal thin film.

[0074] Moreover, according to this invention, the piezo electric crystal thin film excellent in the

piezo electric crystal property can be offered by preventing lowering of the oxygen density in a piezo electric crystal thin film.

[0075] Furthermore, according to this invention, although the actuator equipped with this piezo electric crystal thin film, especially an ink jet type recording head are offered, it can do.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the manufacture approach of a piezo electric crystal thin film. Furthermore, this invention relates to the piezo electric crystal thin film obtained using this manufacture approach, and the actuator using this.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] This actuator transforms electric energy into mechanical energy, or performs that reverse, and is used for a pressure sensor, a temperature sensor, an ink jet type recording head, etc. In the ink jet type recording head, the piezo electric crystal thin film is used as vibrator used as the driving source of the ink regurgitation.

[0003] This piezo electric crystal thin film has the structure generally equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode. Generally the presentation of this piezo electric crystal thin film is made into the binary system which uses titanite-acid lead zirconate (henceforth "PZT") as a principal component, or the three-component system which added the third component to PZT of this binary system.

[0004] The piezo electric crystal thin film of these presentations can be formed with a sputter, a sol gel process, the laser ablation method, or a CVD method.

[0005] The ferroelectric using binary system PZT as these examples is indicated by "Applied Physics Letters, 1991, Vol.58, No.11, and pages 1161-1163." Moreover, JP,6-40035,A and the piezo electric crystal which used binary system PZT for "Journal of The American Ceramic Society, 1973, Vol.56, No.2, and pages 91-96" are indicated.

[0006] When applying said piezo electric crystal thin film to for example, an ink jet type recording head, a piezo electric crystal thin film (PZT film) equipped with 0.4 micrometers - about 20 micrometers thickness is desired. Furthermore, since a high piezoelectric strain constant is required of this piezo electric crystal thin film, it heat-treats at the temperature of 700 degrees C or more, and it is usually supposed that it is required to grow up the crystal grain of this piezo electric crystal thin film.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to the manufacture approach of the piezo electric crystal thin film concerning this invention, in the process which forms a piezo electric crystal thin film, the piezo electric crystal thin film excellent in the piezo electric crystal property can be offered by preventing lowering of the oxygen density in a piezo electric crystal thin film.

[0074] Moreover, according to this invention, the piezo electric crystal thin film excellent in the piezo electric crystal property can be offered by preventing lowering of the oxygen density in a piezo electric crystal thin film.

[0075] Furthermore, according to this invention, although the actuator equipped with this piezo electric crystal thin film, especially an ink jet type recording head are offered, it can do.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, this invention person came to acquire the knowledge of the oxygen density in a piezo electric crystal thin film falling, and degrading a piezoelectric strain constant by this heat treatment. Then, the following judgments were acquired when this invention person examined this reason wholeheartedly. That is, the platinum used as the bottom electrode of a piezo electric crystal thin film is rich in the property to adsorb oxygen so that clearly from it being what is used as an oxidation catalyst.

[0008] Therefore, a bottom electrode is made combined with the titanium which carried out the trap of the oxygen in PZT when PZT was sintered, and has been diffused in a bottom electrode.

[0009] Then, this invention aims at offering the manufacture approach of a piezo electric crystal thin film excellent in the piezo electric crystal property in the process which forms a piezo electric crystal thin film by preventing lowering of the oxygen density in a piezo electric crystal thin film, in order to solve such a technical problem.

[0010] Other objects of this invention are offering such a piezo electric crystal thin film. The object of further others of this invention is offering the actuator equipped with this piezo electric crystal thin film, especially an ink jet type recording head.

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MEANS

[Means for Solving the Problem] In order to attain this object, this invention forms a top electrode and a bottom electrode on both sides of the piezo electric crystal film which consists of the polycrystalline substance, and is characterized by heat-treating under an oxygen ambient atmosphere before after [said bottom electrode formation] piezo electric crystal thin film formation in the manufacture approach of the piezo electric crystal thin film which carries out the formation postheat treatment of said piezo electric crystal on a bottom [this] electrode. Said oxygen ambient atmosphere is desirable and oxygen tension is 60% or more of range (with volume ratio). When oxygen tension is less than 100%, other gas is nitrogen or an argon.

[0012] Furthermore, in the piezo electric crystal thin film equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode, before the piezo electric crystal thin film concerning this invention forms a piezo electric crystal thin film on said bottom electrode, it heat-treats and said bottom electrode consists of under oxygen existence.

[0013] Moreover, other piezo electric crystal thin films concerning this invention are characterized by the oxygen ratio of concentration (r) of the oxygen density in the piezo electric crystal thin film near said bottom electrode and a piezo electric crystal thin film being in or more 0.9 1.2 or less range in the piezo electric crystal thin-film thing equipped with the piezo electric crystal film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal film and a bottom electrode. Here, an oxygen density (r) is displayed as follows. Near means less than $10 \times 10^{-9} \text{m}$.

[0014] $r = (\text{oxygen density in the piezo electric crystal film the oxygen density} / \text{near the bottom electrode})$ [in a piezo electric crystal thin film]

Furthermore, this invention is characterized by being the actuator which uses said piezo electric crystal thin film as a mechanical stress generating means. Furthermore, this invention is characterized by being the ink jet type recording head equipped with said actuator.

[0015]

[Embodiment of the Invention] Next, the gestalt of operation concerning this invention is explained with reference to a drawing. In addition, the gestalt of this operation explains the case where the PZT film is formed as piezo electric crystal film.

[0016] (Gestalt 1 of operation) Drawing 1 is the sectional view showing the configuration of the piezo electric crystal component concerning this invention. This piezo electric crystal thin film is equipped with the electrode 16 after being formed on a silicon substrate 11, the silicon oxide 12 formed on the silicon substrate 11, the PZT film 15 formed on silicon oxide the titanium film (Ti/TiO₂/Ti) 13 formed 12 top and the bottom electrode (Ti/Pt) 14, and the PZT film 15, and is constituted.

[0017] Said bottom electrode 14 is formed from the platinum combined with the layer of titanium and titanium oxide like previous statement at the time of film production. By making the bottom electrode 14 such a configuration, since it says that the lattice constant of the bottom electrode 14 and the lattice constant of the PZT film 15 can carry out near, adhesion with the PZT film 15 formed in behind can be raised.

[0018] The titanium layer which consists of (Ti/TiO₂/Ti) is formed for raising the adhesion

between silicon oxide and a platinum layer on silicon oxide 12. Furthermore, Ti is formed on platinum for making a piezo-electric thin film into a columnar structure like the after-mentioned. [0019] this invention persons have proposed from sometime past that a piezo electric crystal property can be improved by making the crystal structure of a piezo electric crystal thin film into a columnar structure. The crystal structure of a piezo electric crystal thin film can be adjusted to structure which raises a piezo electric crystal property by forming titanium in the shape of an island on platinum.

[0020] In addition, (Ti/TiO₂/Ti) of the titanium film is not observed with a scanning electron microscope by annealing performed after PZT film production as what is spread in Pt or SiO₂ and forms a layer special on a bottom electrode, either.

[0021] The PZT film 15 consists of the polycrystalline substance, and the grain boundary of this crystalline exists in the abbreviation perpendicular direction to the flat surface of the vertical electrodes 14 and 16, as shown in drawing 3 and drawing 4. That is, the crystal grain of PZT has accomplished the columnar structure.

[0022] That to which this PZT film 15 uses binary system as a principal component, and the thing which uses as a principal component three-component system which added the third component to this binary system are used suitably. What has the presentation expressed with the chemical formula of Pb(Zr_xTi_{1-x})O₃+YPbO (being here 0.40≤X≤0.6, 0≤Y≤0.3) as a desirable example of binary system PZT is mentioned.

[0023] Moreover, as a desirable example of three-component system PZT, what has the presentation expressed with the chemical formula shown in the following which added the third component is mentioned to PZT of said binary system.

[0024]

PbTiaZrb(AgBh) cO₃+ePbO+(fMgO)_n (here, A expresses the trivalent metal chosen from the group which consists of a divalent metal chosen from the group which consists of Mg, Co, Zn, Cd, Mn, and nickel, or Sb, Y, Fe, Sc, Yb, Lu, In and Cr.) Moreover, B expresses the pentavalent metal chosen from the group which consists of Nb, Ta, and Sb, or the metal of 6 ** chosen from the group which consists of W and Te. Moreover, although it is a+b+c=1, 0.35≤a≤0.55, 0.25≤b≤0.55, 0.1≤c≤0.4, 0≤e≤0.3, 0≤f≤0.15c, g=f/2, and n= 0 however, A — a trivalent metal — it is — and B — the metal of 6 ** — not but — moreover, the case where g is 1/3, and h is 2/3, and Mg and B of A are Nb(s) when A is a divalent metal and B is a pentavalent metal — as long as — n expresses 1.

As a more desirable example of three-component system, magnesium lead niobate, i.e., A, is Mg, B is Nb, and that 1/whose 3h g is 2/3 is mentioned.

[0025] Furthermore, even if it is any of these binary system PZT and three-component system PZT, in order to improve the piezo-electric property, Ba, Sr, La, Nd, Nb, Ta, Sb, Bi, W, Mo, calcium, etc. of a minute amount may be added. In three-component system, addition of Sr not more than 0.10 mol % and Ba is especially much more desirable to an improvement of a piezo-electric property. Moreover, since addition of Mn not more than 0.10 mol % and nickel improves the degree of sintering in three-component system, it is desirable.

[0026] In the process which forms the piezo electric crystal thin film 15, in order to acquire structure like previous statement, predetermined heat treatment is performed. According to the place which this invention persons examined, the oxygen in PZT is spread in a bottom electrode in the case of this heat treatment. If a bottom electrode is formed by sputtering so that it may mention later, it will check that an electrode has a columnar structure like PZT. In this crystal structure, the inclination for the trap of the oxygen to be carried out to a grain boundary is strong, and the titanium diffused in platinum forms an oxide in this grain boundary.

[0027] Then, this invention person proposed forming heat treatment for a bottom electrode under oxygen existence, before annealing PZT, as shown below. Drawing 4 is the scanning microphotography which shows the cross section of the cross direction of the piezo electric crystal thin film formed by the approach described below, and was obtained under conditions with an acceleration voltage [of 15kV], and a cash-drawer electrical potential difference of 4.0kV.

[0028] According to this, it turns out that a bottom electrode and the piezo electric crystal film have the pillar-shaped crystal structure mostly mentioned already. The trap of the oxygen in a

piezo electric crystal thin film is carried out to each grain boundary in a bottom electrode. Moreover, it has appeared as a round grain which the compound of the oxygen and Ti which were diffused in platinum is among a bottom electrode, and carried out division-into-equal-parts powder by heat treatment under the oxygen ambient atmosphere of a bottom electrode.

[0029] Next, the manufacture approach of the piezo electric crystal thin film concerning 1 operation gestalt of this invention is explained with reference to a drawing.

[0030] Drawing 5 (a) thru/or drawing 5 (c) are the sectional views showing the production process of the piezo electric crystal thin film mentioned above. At the process shown in drawing 5 (a), it oxidizes thermally to a silicon substrate 11, and the silicon oxide 12 whose thickness is about 0.3–1.2 micrometers is formed on a silicon substrate 11. Next, the thickness as the whole forms the titanium film 13 which consists of Ti/TiO₂/Ti (0.01 micrometers thru/or about 0.04 micrometers) on silicon oxide 12 by the spatter. Subsequently, the bottom electrode 14 which consists of platinum is formed by about 0.2–0.8–micrometer thickness on the titanium film 13 by the spatter.

[0031] The spatter conditions at this time are as follows. The direct-current sputtering system was used as equipment. A spatter flow and pressure requirement is 0.4Pa. In Pt, electrical-potential-difference conditions are 1kw(s), and, in the case of Ti, it is 200w, and, in TiO₂, is 300w. In the case of Pt and Ti, the conditions of a controlled atmosphere are among an argon, and, in TiO₂, it is O₂/Ar=10/90.

[0032] subsequently, the component in the middle of this film production — a diffusion furnace — putting in — the bottom of an oxygen ambient atmosphere (60% or more of oxygen tension), 400, or 600 degrees C — 30 — or it heats for 60 minutes. or a RTA (Rapid Thermal Annealing) furnace — this component — putting in — the inside of an oxygen ambient atmosphere (flow rate 5 L/min) — temperature 400 thru/or 600 degrees C — time amount — 60 — or it heats for 300 seconds.

[0033] Next, titanium is formed in the shape of an island by the spatter on the bottom electrode 14 formed at the process shown in drawing 5 (a) like the process shown in drawing 5 (b). Orientation of the crystal structure of a piezo electric crystal thin film can be strongly carried out to the 100th page by making this titanium into 40 thru/or 60A thickness.

[0034] Subsequently, this PZT film 15 is produced on this. This is performed with a sol gel process. Here, suppose that PZT is manufactured with the multilayer coat of two coats 8 times using a sol gel process. This sol gel process is as follows.

[0035] This manufacture approach is an approach of carrying out dehydration processing of the hydration complex of the hydroxide of the metal component which can form the PZT film 15, i.e., the sol, considering as gel, carrying out heating baking of this gel, and adjusting an inorganic oxide. This manufacture approach consists of each following process.

[0036] a. In the gestalt of membrane formation process book operation of a sol constituent, the sol of the metal component which constitutes the PZT film can hydrolyze and adjust from an acid the metaled alkoxide or the acetate which can form the PZT film. In this invention, the presentation of the PZT film mentioned above can be acquired by controlling the presentation of the metal in a sol. That is, let titanium, a zirconium, lead, each alkoxide of the metal component of further others, or acetate be a start raw material.

[0037] Here, there is an advantage that the presentation of the metal component which will constitute the PZT film by the time it considers as the PZT film (piezo electric crystal thin film) eventually is maintained mostly. That is, the presentation of a metal component [in / there are very little metal component and fluctuation especially according to evaporation of a lead component etc. during baking and annealing treatment, therefore / these start raw materials] will be in agreement with the metal presentation in the PZT film obtained eventually. That is, the presentation of gel is determined according to the piezo electric crystal film (the gestalt of this operation PZT film) which it is going to generate.

[0038] Moreover, in order to obtain the PZT film with which the lead component mentioned above becomes superfluous with the gestalt of this operation, 15–mol the thing carried out to an excess to % is preferably more desirable than the amount of which a lead component is required from a stoichiometry in a sol to 20–mol %.

[0039] As for this sol, with the gestalt of this operation, it is desirable to be used as a constituent mixed with the organic high molecular compound. This organic high molecular compound prevents

effectively that absorb the residual stress of a thin film at the time of desiccation and baking, and a crack arises in this thin film. If the gel containing this organic macromolecule is specifically used, pore will arise in the gelled thin film which is mentioned later. It is thought that this pore absorbs the residual stress of a thin film in pre annealing and the annealing process which are mentioned further later. Here, as an organic high molecular compound used preferably, polyvinyl acetate, hydroxypropylcellulose, a polyethylene glycol, the polyethylene-glycol monomethyl ether, a polypropylene glycol, polyvinyl alcohol, polyacrylic acid, a polyamide, the poly AMIKU acid, an acetyl cellulose, its derivative, and those copolymers are mentioned.

[0040] In addition, with the gestalt of this operation, the porosity gel thin film which is 1 micrometer or less in magnitude, and had large distribution can be formed by adding hydroxypropylcellulose for the porosity gel thin film which has much about 0.05-micrometer pores by adding polyvinyl acetate.

[0041] With the gestalt of this operation, a with an average molecular weight of about 285 to 420 thing is suitably used as a polyethylene glycol. Moreover, as a polypropylene glycol, a with an average molecular weight of about 300 to 800 thing is used suitably.

[0042] By the manufacture approach concerning the gestalt of this operation, this sol constituent is first applied on the bottom electrode 14 (refer to drawing 5 (b)) which is going to form the PZT film 15. Especially the method of application at this time is not limited, but the approach usually performed, for example, a spin coat, a DIP coat, a roll coat, a bar coat, etc. can perform it. Moreover, it can also apply by flexographic printing, screen-stencil, offset printing, etc.

[0043] Moreover, when the process after it is taken into consideration, as for the thickness of the film formed of said spreading, it is desirable to control so that the thickness of the porosity gel thin film formed in the gelation process mentioned later is set to 0.3 micrometers or less, and it is good to be more preferably referred to as about 0.2 micrometers.

[0044] Next, the applied sol constituent is heated at air drying or the temperature of 200 degrees C or less. Here, said sol constituent can be further applied on this film dried (heating), and thickness can also be thickened. In this case, as for the film used as a substrate, it is desirable to dry at the temperature of 80 degrees C or more.

[0045] b. Calcinate the film obtained at the gelation process of the film which consists of a sol constituent, next the membrane formation process of a sol constituent mentioned above, and form the porosity gel thin film which consists of an amorphous metallic oxide which does not contain the residual organic substance substantially.

[0046] Baking is sufficient temperature to gel the film of a sol constituent and remove the organic substance out of the film, and is performed by [sufficient] carrying out time amount heating. It is desirable to make burning temperature into 300-450 degrees C with the gestalt of this operation, and it is still more desirable to make it 350-400 degrees C.

[0047] Although it changes with temperature and the formats of a furnace to be used, when a cleaning furnace is used for example, about 10 - 120 minutes of firing time are desirable, and it is more desirable to consider as about 15 - 60 minutes. Moreover, when a hot plate is used, about 1 - 60 minutes is desirable, and it is still more desirable to consider as about 5 - 30 minutes.

[0048] Of the above process, the porosity gel thin film was formed on the bottom electrode 14.

[0049] c. Carry out heating baking of the porosity gel thin film obtained at the pre annealing process, next the process b mentioned above, and change this film into the film which consists of a metal oxide film of a crystalline substance.

[0050] What is necessary is not to perform baking until a perovskite mold crystal occupies most during a crystal, and just to terminate it, when a gel thin film crystallizes to homogeneity although carried out at temperature required in order to change a porosity gel thin film into the film which consists of a metallic oxide of a crystalline substance. With the gestalt of this operation, as a burning temperature, the range of 400-800 degrees C is desirable, and it is more desirable to calcinate in the range which is 550-750 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when using an annealing furnace, for example, about 0.1 - 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 - 2 hours] Moreover, when a RTA (Rapid Thermal Annealing) furnace is used, about 0.1 - 10 minutes is desirable, and about 1 - 5 minutes is more desirable.

[0051] Moreover, with the gestalt of this operation, this pre annealing process can be divided into two steps, and can be carried out. As a first stage story, annealing can be performed at the temperature of the range of 400–600 degrees C, next, specifically, annealing can be first performed at the temperature of the range of 600–800 degrees C as a second stage story. Furthermore, as a first stage story, annealing can be performed at the temperature of the range of 450–550 degrees C, next annealing can be preferably performed at the temperature of the range of 600–750 degrees C as a second stage story.

[0052] According to this process, the porosity gel thin film was transformed to the film which consists of a metal oxide film of a crystalline substance.

[0053] d. It consists of a metal oxide film according to the pre annealing process of Process C, and carry out film conversion, after repeating the processes a and b mentioned above further 3 times a repeat process, next henceforth and carrying out the four-layer laminating of the porosity gel thin film. Subsequently, island-like titanium is formed in the shape of an island by the approach as stated above on PZT, and the processes a and b as stated above are repeated further 4 times.

[0054] What is necessary is just to determine suitably the number of laminatings of the cascade screen obtained as a result of this repeat process in consideration of the thickness of the final PZT film 15. Here, it is good that it is 0.15 micrometers of hits much more. In addition, it cannot be overemphasized that it is desirable that it is the thickness which a crack etc. does not generate in degree process (process e) mentioned later.

[0055] At this repeat process, the porosity gel thin film which newly formed the porosity gel thin film and was newly formed on the film formed previously as a result of subsequent pre annealing turns into film formed previously and film unified substantially.

[0056] Here, a discontinuity layer may be not only when there is no discontinuity layer between the layers by which the laminating was carried out to the film unified substantially but between the layers by which the laminating was carried out unlike the case of the PZT film 15 concerning the gestalt of this operation obtained eventually. And in repeating Processes a, b, and c further, a still newer porosity gel thin film is formed, and this new porosity gel thin film turns into film substantially united with the cascade screen of the crystalline substance obtained above as a result of subsequent pre annealing.

[0057] e. Perform annealing on the film obtained at the perovskite mold crystal growth process, next said process d in 800–1000 degrees C still more preferably the burning temperature of 600–1200 degrees C. Although it changes with burning temperature and the formats of a furnace to be used, when an annealing furnace is used for example, about 0.1 – 5 hours of firing time are desirable, and it is more desirable. [of about 0.5 – 2 hours] Moreover, when a RTA furnace is used, about 0.1 – 10 minutes is desirable, and about 0.5 – 3 minutes is more desirable.

[0058] Moreover, with the gestalt of this operation, this perovskite mold crystal growth process, i.e., annealing, is divided into two steps, it is carried out, and is made. Annealing is performed at the temperature of about 600–800 degrees C, and, specifically, the temperature of 800–1000 degrees C performs annealing on a second stage story on a first stage story. Furthermore, preferably, annealing can be performed at the temperature of about 600–750 degrees C, and the temperature of 800–950 degrees C can perform annealing on a second stage story on a first stage story.

[0059] Of the above actuation, PZT whose thickness which consists titanium of the polycrystalline substance of the shape of a column which grew as a nucleus is 1.2 micrometers is formed on the bottom electrode 14.

[0060] Next, it precedes forming the piezo electric crystal thin film after bottom electrode formation, and the comparison of a piezo-electric property with the case (comparison method) where it is made the same conditions is shown [all of the case (this invention method) where previous statement is heat-treated, and except for having not performed it].

[0061]

	圧電定数 d_{31}	出力係数 g_{31}	誘電率
本発明法	150 (pC/N)	11.2	1500
従来法	120 (pC/N)	9.0	1500

Thus, according to this invention method, the piezo electric crystal thin-film which excelled [all] in the piezo-electric property as compared with the conventional method can be obtained. When this invention person measured the oxygen density in a piezo electric crystal thin film, and the oxygen density in the piezo electric crystal film near 10nm near the bottom electrode in the piezo electric crystal thin film obtained by this invention method, the oxygen density in the piezo electric crystal film near the bottom electrode was large as compared with it in a piezo electric crystal thin film, and it checked that said ratio (r) had been 0.95. Moreover, the oxygen density in the piezo electric crystal film near the bottom electrode was 35 atoms %.

[0062] When this invention person inquires wholeheartedly, as for the ratio (r) of both oxygen density, it is desirable that it is the range of 0.9 thru/or 1.2, and, as for the oxygen density of the inside near the bottom electrode, it is desirable that it is the range of 30 thru/or 60 atom %. On the other hand, a ratio (r) is about 0.67 and, as for these properties of a conventional method, unlike this invention, lowering of the oxygen density in the PZT film was observed notably. In addition, measurement of these oxygen densities was performed as follows.

[0063] The thin film fragmentation of the piezo electric crystal thin film was carried out with the low angle ion milling system, and the component analysis of this was carried out in TEM (transmission electron microscope). the used equipment and low angle ion milling — Japan Fiji tech and — Hang lei It is made in Linda and TEM is Philip FEG-CM200TEM. In addition, the applied voltage in the case of the XEDX observation by TEM is 200kV.

[0064] A measurement result is data which took the average of four points, and is as follows.

[0065]

	PZT膜中	下電極近傍
本発明	33.8	35.3
従来	26.4	39.2

(The unit of data is atomic %.)

According to this invention, a piezoelectric constant (d31) can be improved 20 to 30% compared with the conventional thing.

[0066] The process of drawing 5 (b) is ended by the above, and it shifts to the process shown in drawing 5 (c) below. At this process, thickness forms the electrode 16 when consisting of about 0.2–1.0–micrometer aluminum by the spatter on the PZT film 15 obtained at the process shown in drawing 5 (b).

[0067] Thus, the piezo electric crystal thin film as shown in drawing 2 was obtained. In addition, it was checked that there is no generating of a crack in the obtained PZT film 15, and the surface of discontinuity of the shape of a layer by the laminating does not exist in a cross section, either.

[0068] Drawing 6 is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[0069] The ink jet type recording head concerning the gestalt 3 of operation The silicon substrate 21 in which the ink reservoir 27 was formed as shown in drawing 6 , The diaphragm 22 formed on the silicon substrate 21, and the bottom electrode 23 formed in the request location on a diaphragm 22, It is on the bottom electrode 23, and it has the piezo electric crystal thin film 24 formed in the location corresponding to the ink reservoir 27, the electrode 25 after being formed on the piezo electric crystal thin film 24, and the 2nd substrate 26 joined to the underside of a silicon substrate 21, and is constituted.

[0070] The bottom electrode 23 has the same configuration as the bottom electrode explained with the gestalt 2 of operation. Moreover, the piezo electric crystal thin film 24 has the same configuration as the PZT film explained with the gestalt 1 of operation.

[0071] Ink is supplied to the ink reservoir 27 through the ink passage which does not illustrate this ink jet type recording head. Here, if an electrical potential difference is impressed to the piezo electric crystal film 24 through the bottom electrode 23 and the top electrode 25, the piezo electric crystal film 24 will deform and a pressure will be applied to the ink in the ink reservoir 27. It is breathed out by this pressure from the nozzle which ink does not illustrate, and ink jet record is performed with it.

[0072] Since the piezo electric crystal thin film excellent in the piezo-electric property as stated above is used for this ink jet type recording head as vibrator, it can make ink breathe out by the big pressure here.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the piezo electric crystal thin film concerning the gestalt 1 of operation of this invention.

[Drawing 2] It is the scanning electron microscope (SEM) photograph in which the cross section of the PZT film which constitutes the piezo electric crystal thin film concerning the gestalt 1 of operation is shown.

[Drawing 3] It is the scanning electron microscope photograph in which the flat surface of the PZT film shown in drawing 2 is shown.

[Drawing 4] It is the scanning microscope (SEM) photograph in which the cross section of the piezo electric crystal thin film obtained according to the production process of this invention is shown.

[Drawing 5] (a) Or (c) is the sectional view showing the production process of the piezo electric crystal thin film mentioned above.

[Drawing 6] It is the sectional view showing one ink reservoir part of the ink jet type recording head which used the piezo electric crystal thin film concerning this invention as a trembler.

[Description of Notations]

11 21 Silicon substrate

12 Silicon Oxide

13 Titanic-Acid-ized Film

14 23 Bottom electrode

14B Titanium seed crystal

15 PZT Film

16 25 Top electrode

22 Diaphragm

24 Piezo Electric Crystal Thin Film

26 Substrate

27 Ink ***

[Translation done.]

*** NOTICES ***

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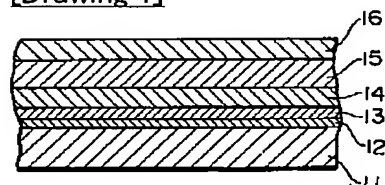
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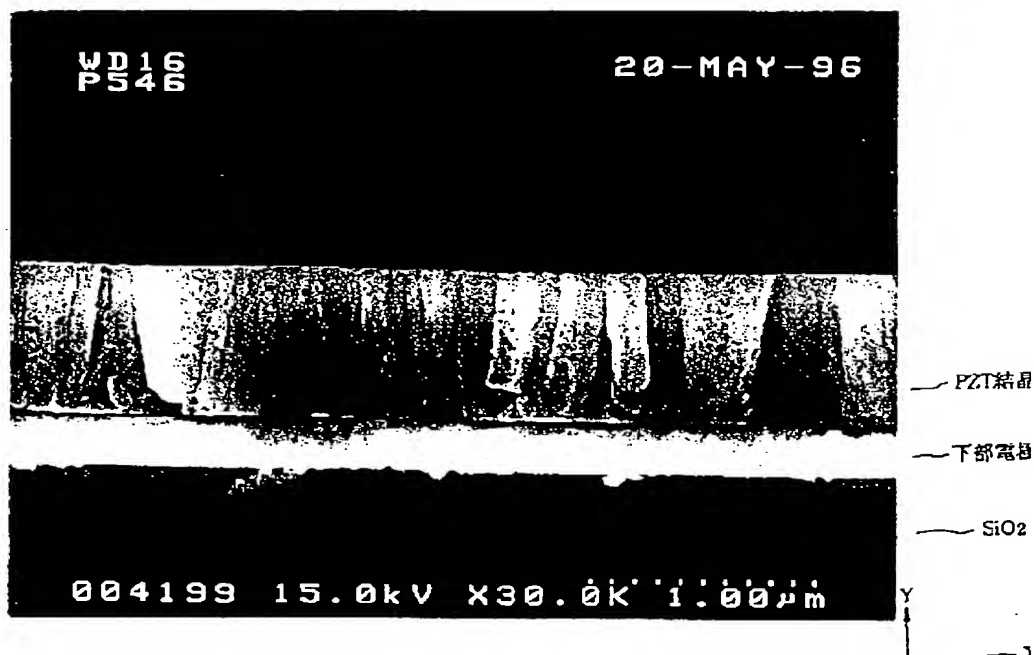
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DRAWINGS

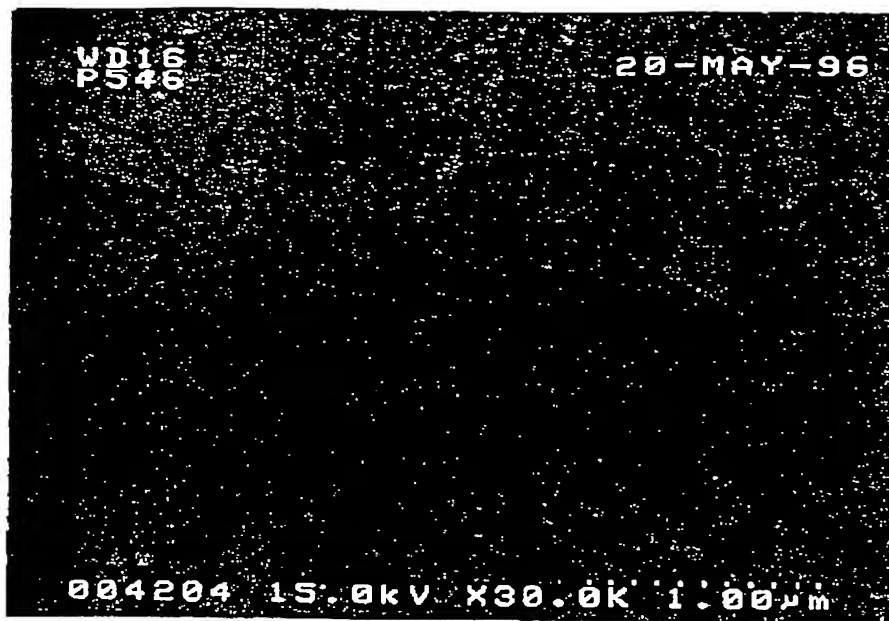
[Drawing 1]



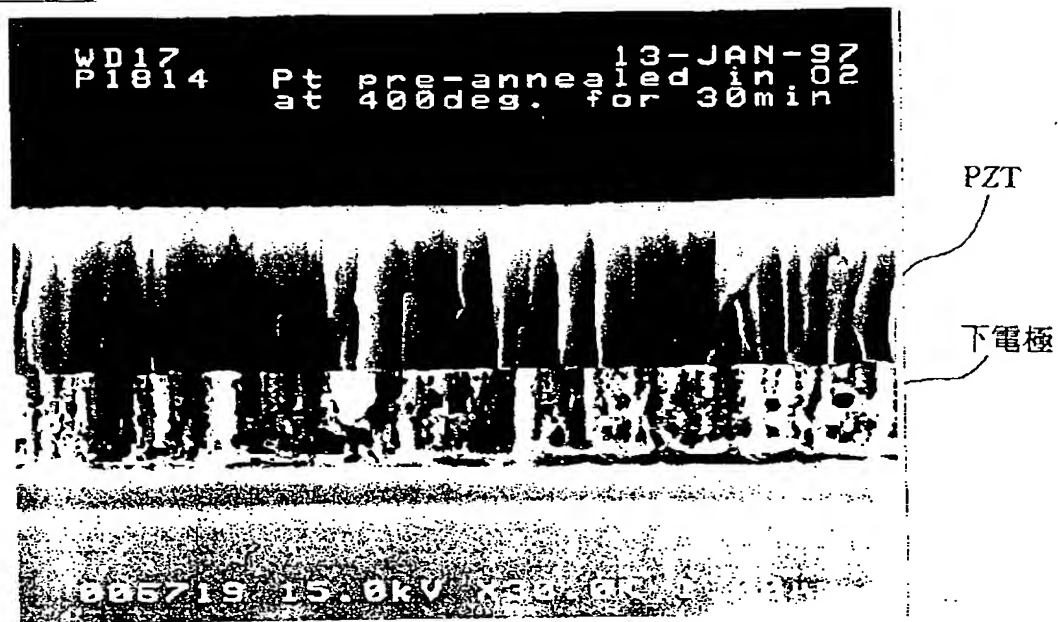
[Drawing 2]



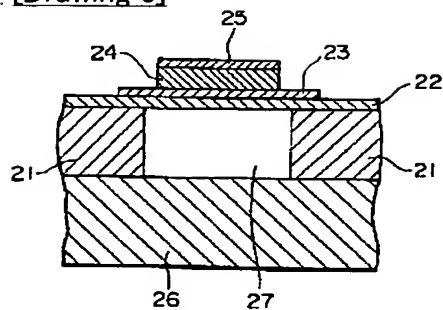
[Drawing 3]



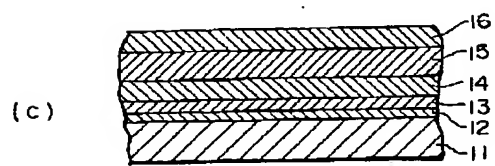
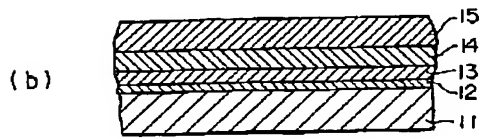
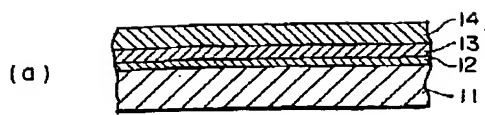
[Drawing 4]



[Drawing 6]



[Drawing 5]



[Translation done.]

* NOTICES *

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CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by the convention of 2 of Article 17 of Patent Law
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H01L 41/08 C

H01L 41/22 Z

B41J 3/04 103 A

B41J 3/04 103 H

[Procedure amendment]

[Filing Date] April 15, Heisei 16 (2004. 4.15)

[Procedure amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claim

[Method of Amendment] Modification

[The content of amendment]

[Claim(s)]

[Claim 1]

The manufacture approach of the piezo electric crystal thin film characterized by heat-treating under an oxygen ambient atmosphere before after [said bottom electrode formation] piezo electric crystal thin film formation in the manufacture approach of the piezo electric crystal thin film which consists of a top electrode and a bottom electrode on both sides of a piezo electric crystal thin film, and carries out the formation postheat treatment of said piezo electric crystal thin film on the bottom electrode concerned.

[Claim 2]

The approach according to claim 1 said oxygen ambient atmosphere is 60% or more of oxygen tension.

[Claim 3]

The piezo electric crystal thin film which comes to heat-treat said bottom electrode under oxygen existence in the piezo electric crystal thin film equipped with the piezo electric crystal thin film

which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode before forming a piezo electric crystal thin film on said bottom electrode.

[Claim 4]

The piezo electric crystal thin film characterized by the oxygen ratio of concentration the oxygen density of the piezo electric crystal thin film near said bottom electrode and in the middle of a piezo electric crystal thin film (r) being in or more 0.9 1.2 or less range in the piezo electric crystal thin film equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode.

$r = (\text{oxygen density in the piezo electric crystal thin film the oxygen density} / \text{near the bottom electrode}) [\text{in the middle of a piezo electric crystal thin film}]$

[Claim 5]

The piezo electric crystal thin film to which said bottom electrode is characterized by oxygen existing the crystal structure of a columnar structure in nothing and its grain boundary in said piezo electric crystal thin film according to claim 3 or 4.

[Claim 6]

The actuator which uses said claim 3 thru/or the piezo electric crystal thin film of any one publication of five as a mechanical stress generating means.

[Claim 7]

The ink jet type recording head equipped with said actuator according to claim 7.

[Procedure amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0011

[Method of Amendment] Modification

[The content of amendment]

[0011]

[Means for Solving the Problem]

In order to attain this object, this invention consists of a top electrode and a bottom electrode on both sides of a piezo electric crystal thin film, and is characterized by heat-treating under an oxygen ambient atmosphere before after [said bottom electrode formation] piezo electric crystal thin film formation in the manufacture approach of the piezo electric crystal thin film which carries out the formation postheat treatment of said piezo electric crystal thin film on the bottom electrode concerned. Said oxygen ambient atmosphere is desirable and oxygen tension is 60% or more of range (with volume ratio). When oxygen tension is less than 100%, other gas is nitrogen or an argon.

[Procedure amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0012

[Method of Amendment] Modification

[The content of amendment]

[0012]

Furthermore, in the piezo electric crystal thin film equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode, before forming a piezo electric crystal thin film on said bottom electrode, said bottom electrode is heat-treated under oxygen existence, and it is constituted.

[Procedure amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0013

[Method of Amendment] Modification

[The content of amendment]

[0013]

Moreover, other piezo electric crystal thin films concerning this invention are characterized by the

oxygen ratio of concentration the oxygen density of the piezo electric crystal thin film near said bottom electrode and in the middle of a piezo electric crystal thin film (r) being in or more 0.9 1.2 or less range in the piezo electric crystal thin film equipped with the piezo electric crystal thin film which consists of the polycrystalline substance, and an electrode when arranged on both sides of this piezo electric crystal thin film and a bottom electrode. Here, an oxygen density (r) is displayed as follows. In addition, near means less than $10 \times 10^{-9} \text{m}$. Here, it considers as $r = (\text{oxygen density in the piezo electric crystal film the oxygen density} / \text{near the bottom electrode})$. [in a piezo electric crystal thin film] Furthermore, in the above-mentioned piezo electric crystal thin film, said bottom electrode is characterized by oxygen existing the crystal structure of a columnar structure in nothing and its grain boundary.

[Procedure amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0014

[Method of Amendment] Modification

[The content of amendment]

[0014]

Furthermore, this invention is characterized by being the actuator which uses said piezo electric crystal thin film as a mechanical stress generating means. Furthermore, this invention is characterized by being the ink jet type recording head equipped with said actuator.

[Procedure amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0016

[Method of Amendment] Modification

[The content of amendment]

[0016]

(Gestalt 1 of operation)

Drawing 1 is the sectional view showing the configuration of the piezo electric crystal thin film concerning this invention. This piezo electric crystal thin film is equipped with the electrode 16 after being formed on a silicon substrate 11, the silicon oxide 12 formed on the silicon substrate 11, the PZT film 15 formed on silicon oxide the titanium film (Ti/TiO₂/Ti) 13 formed 12 top and the bottom electrode (Ti/Pt) 14, and the PZT film 15 (it is suitably expressed as "the piezo electric crystal thin film 15"), and is constituted.

[Procedure amendment 7]

[Document to be Amended] Description

[Item(s) to be Amended] 0061

[Method of Amendment] Modification

[The content of amendment]

[0061]

圧電定数 d_{31}	出力係数 g_{31}	誘電率	
本発明法	150 (pC/N)	11.2	1500
従来法	120 (pC/N)	9.0	1500

Thus, according to this invention method, the piezo electric crystal thin film which excelled [all] in the piezo-electric property as compared with the conventional method can be obtained. When this invention person measured the oxygen density in the middle of a piezo electric crystal thin film, and the oxygen density in the piezo electric crystal film near 10nm near the bottom electrode in the piezo electric crystal thin film obtained by this invention method, the oxygen density in the piezo electric crystal film near the bottom electrode was large as compared with it in the middle of

a piezo electric crystal thin film, and it checked that said ratio (r) had been 0.95. Moreover, the oxygen density in the piezo electric crystal film near the bottom electrode was 35 atoms %.

[Translation done.]

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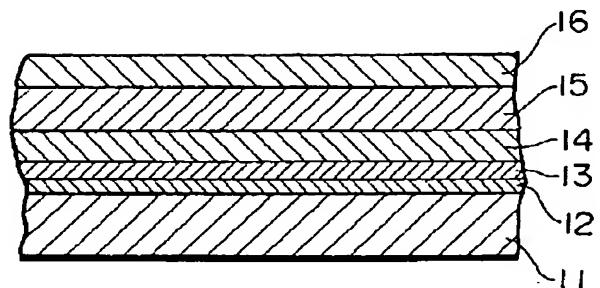
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(54) 【発明の名称】 圧電体薄膜素子、これを用いたアクチュエータ、インクジェット式記録ヘッド、並びに圧電体薄膜素子の製造方法

(57) 【要約】

【課題】 圧電体薄膜素子を形成する過程において、圧電体薄膜中の酸素濃度の低下を防ぐことにより、圧電体特性に優れた圧電体薄膜の製造方法を提供する。

【解決手段】 多結晶体からなる圧電体膜15を挟んで上電極16と下電極14とを形成し、この下電極上に前記圧電体を形成後熱処理する圧電体薄膜の製造方法であって、前記下電極形成後圧電体薄膜形成前に酸素雰囲気下で熱処理する。



【特許請求の範囲】

【請求項1】 圧電体膜を挟んで上電極と下電極とを形成するものであって、この下電極上に前記圧電体を形成後熱処理する圧電体薄膜の製造方法において、前記下電極形成後圧電体薄膜形成前に酸素雰囲気下で熱処理することを特徴とする圧電体薄膜の製造方法。

【請求項2】 前記酸素雰囲気が、酸素分圧60%以上である請求項1記載の方法。

【請求項3】 多結晶体からなる圧電体膜と、該圧電体膜を挟んで配置される上電極と下電極と、を備えた圧電体薄膜素子において、前記下電極上に圧電体薄膜を形成する前に、前記下電極を酸素存在下で熱処理してなる圧電体薄膜素子。

【請求項4】 多結晶体からなる圧電体膜と、該圧電体膜を挟んで配置される上電極と下電極と、を備えた圧電体薄膜素子において、前記下電極近傍の圧電体の酸素濃度と圧電体薄膜の酸素濃度比（ r ）が0.9以上1.2以下の範囲にあることを特徴とする圧電体薄膜素子。

$r = (\text{圧電体薄膜中の酸素濃度} / \text{下電極近傍の圧電体膜中の酸素濃度})$

【請求項5】 前記請求項3又は4記載の圧電体薄膜素子を機械的応力発生手段として利用するアクチュエータ。

【請求項6】 前記請求項5記載のアクチュエータを備えたインクジェット式記録ヘッド。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は圧電体薄膜素子の製造方法に関するものである。さらに、本発明は、この製造方法を用いて得られた圧電体薄膜素子、及びこれを用いたアクチュエータに関するものである。

【0002】

【従来の技術】このアクチュエータは電気的エネルギーを機械的エネルギーに変換し、またはその逆を行うものであって、圧力センサ、温度センサ、インクジェット式記録ヘッド等に用いられる。インクジェット式記録ヘッドでは、圧電体薄膜素子をインク吐出の駆動源となる振動子として用いている。

【0003】この圧電体薄膜素子は、一般的に、多結晶体からなる圧電体薄膜と、この圧電体薄膜を挟んで配置される上電極及び下電極と、を備えた構造を有している。この圧電体薄膜の組成は、一般的に、チタン酸ジルコン酸鉛（以下、「PZT」という）を主成分とする二成分系、または、この二成分系のPZTに第三成分を加えた三成分系とされている。

【0004】これらの組成の圧電体薄膜は、例えば、スパッタ法、ゾルゲル法、レーザアブレーション法又はCVD法等により形成することができる。

【0005】これらの例として、二成分系PZTを用いた強誘電体が、"Applied Physics Letters, 1991, Vol.

58, No.11, pages 1161-1163"に記載されている。また、特開平6-40035号公報や、"Journal of The American Ceramic Society, 1973, Vol.56, No.2, pages 91-96"には、二成分系PZTを用いた圧電体が開示されている。

【0006】前記圧電体薄膜素子を、例えばインクジェット式記録ヘッドに適用する場合、0.4 μ m \sim 20 μ m程度の膜厚を備えた圧電体薄膜（PZT膜）が望まれる。さらに、この圧電体薄膜には高い圧電ひずみ定数が要求されるので、通常、700 $^{\circ}$ C以上の温度で熱処理を行い、この圧電体薄膜の結晶粒を成長させることが必要であるとされている。

【0007】

【発明が解決しようとする課題】しかしながら、本発明者は、この熱処理によって圧電体薄膜中の酸素濃度が低下して圧電ひずみ定数を劣化させる、との知見を得るに到った。そこで、本発明者がこの理由について鋭意検討したところ、次のような見解を得た。すなわち、圧電体薄膜素子の下電極となる白金は、酸化触媒として利用されるものであることから明らかなように、酸素を吸着する性質に富んでいる。

【0008】したがって、下電極は、PZTが焼結される際にPZT中の酸素をトラップし、また、下電極中に拡散してきたチタンと結合させることになる。

【0009】そこで、本発明はこのような課題を解決するために、圧電体薄膜素子を形成する過程において、圧電体薄膜中の酸素濃度の低下を防ぐことにより、圧電体特性に優れた圧電体薄膜の製造方法を提供することを目的とする。

【0010】本発明の他の目的は、このような圧電体薄膜を提供することである。本発明のさらに他の目的は、この圧電体薄膜を備えたアクチュエータ、特にインクジェット式記録ヘッドを提供することである。

【0011】

【課題を解決するための手段】この目的を達成するために、本発明は、多結晶体からなる圧電体膜を挟んで上電極と下電極とを形成するものであって、この下電極上に前記圧電体を形成後熱処理する圧電体薄膜の製造方法において、前記下電極形成後圧電体薄膜形成前に酸素雰囲気下で熱処理することを特徴とする。前記酸素雰囲気は、好ましくは、（体積比で）酸素分圧が60%以上の範囲である。酸素分圧が100%未満の場合、他のガスは、例えば、窒素、或いはアルゴンである。

【0012】さらに、本発明に係わる圧電体薄膜素子は、多結晶体からなる圧電体膜と、該圧電体膜を挟んで配置される上電極と下電極と、を備えた圧電体薄膜素子において、前記下電極上に圧電体薄膜を形成する前に、前記下電極を酸素存在下で熱処理をして構成される。

【0013】また、本発明に係わる他の圧電体薄膜素子は、多結晶体からなる圧電体膜と、該圧電体膜を挟んで

配置される上電極と下電極と、を備えた圧電体薄膜素子
ものにおいて、前記下電極近傍の圧電体薄膜中の酸素濃
度と圧電体薄膜の酸素濃度比（ r ）が0.9以上1.2
以下の範囲にあることを特徴とする。ここで、酸素濃度
（ r ）は次のように表示される。近傍とは、例えば、 10×10^{-9} m以内をいう。

【0014】 $r = (\text{圧電体薄膜中の酸素濃度} / \text{下電極近
傍の圧電体膜中の酸素濃度})$

さらに、本発明は、前記圧電体薄膜素子を機械的応力発
生手段として利用するアクチュエータであることを特徴
とする。さらに、本発明は、前記アクチュエータを備え
たインクジェット式記録ヘッドであることを特徴とす
る。

【0015】

【発明の実施の形態】次に、本発明に係る実施の形態に
ついて図面を参照して説明する。なお、本実施の形態で
は、圧電体膜としてPZT膜を形成した場合について説
明する。

【0016】（実施の形態1）図1は本発明に係わる圧
電体素子の構成を示す断面図である。この圧電体薄膜素
子は、シリコン基板11と、シリコン基板11上に形成
されたシリコン酸化膜12と、シリコン酸化膜12上形
成されたチタン膜（Ti/TiO₂/Ti）13と、下電極（Ti/Pt）
14上に形成されたPZT膜15と、PZT膜15上に
形成された上電極16を、備えて構成されている。

【0017】前記下電極14は、既述のように、製膜時
にはチタン及び酸化チタンの層と組み合わされたプラチ
ナから形成されている。下電極14をこのような構成に
することで、下電極14の格子定数とPZT膜15の格
子定数が近くできるという理由から、後に形成するPZ
T膜15との密着性を向上させることができる。

【0018】シリコン酸化膜12上に（Ti/TiO₂/Ti）か
らなるチタン層を形成するのは、シリコン酸化膜と白金層
との間の密着性を高めるためである。さらに、白金上に
Tiを形成するのは、圧電薄膜を後述のように柱状構造に
するためである。

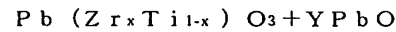
【0019】本発明者らは、圧電体薄膜の結晶構造を柱
状構造にすることにより、圧電体特性を向上できること
をかねてより提案している。チタンを白金上に、島状に
形成することにより圧電体薄膜の結晶構造を圧電体特性
を高めるような構造に調整できる。

【0020】なお、PZT製膜後に行われるアニールによ
って、チタン膜の（Ti/TiO₂/Ti）は、Pt内あるいはS
iO₂内に拡散し下電極の上に特別な層を形成するもの
としては、走査型電子顕微鏡によっても観測されない。

【0021】PZT膜15は多結晶体からなり、この結
晶体の粒界が、図3、図4に示すように、上下電極14
及び16の平面に対して略垂直方向に存在している。す
なわち、PZTの結晶粒が柱状構造を成している。

【0022】このPZT膜15は、二成分系を主成分と

するもの、この二成分系に第三成分を加えた三成分系を
主成分とするものが好適に用いられる。二成分系PZT
の好ましい具体例としては、

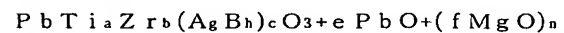


（ここで、 $0.40 \leq x \leq 0.6$, $0 \leq Y \leq 0.3$ ）

の化学式で表わされる組成を有するものが挙げられる。

【0023】また、三成分系PZTの好ましい具体例と
しては、前記二成分系のPZTに、例えば、第三成分を
添加した以下に示す化学式で表わされる組成を有するも
のが挙げられる。

【0024】



（ここで、Aは、Mg, Co, Zn, Cd, Mn及びNi
からなる群から選択される2価の金属またはSb,

Y, Fe, Sc, Yb, Lu, In及びCrからなる群
から選択される3価の金属を表す。また、Bは、Nb,

Ta及びSbからなる群から選択される5価の金属、ま
たはW及びTeからなる群から選択される6価の金属を
表す。また、 $a + b + c = 1$, $0.35 \leq a \leq 0.5$

5 , $0.25 \leq b \leq 0.55$, $0.1 \leq c \leq 0.4$,
 $0 \leq e \leq 0.3$, $0 \leq f \leq 0.15$, $g = f = 1$

$/2$, $n = 0$ であるが、但し、Aが3価の金属であり、
かつBが6価の金属でなく、また、Aが2価の金属であ
り、かつBが5価の金属である場合、 g は $1/3$ であ
り、 h は $2/3$ であり、また、AはMg、BがNbの場
合に限り、 n は1を表す。）

三成分系のより好ましい具体例としては、マグネシウム
ニオブ酸鉛、すなわち、AがMgであり、BがNbであ
り、 g が $1/3$ 、 h が $2/3$ であるものが挙げられる。

【0025】さらに、これら二成分系PZT及び三成分
系PZTのいずれであっても、その圧電特性を改善する
ために、微量のBa, Sr, La, Nd, Nb, Ta,
Sb, Bi, W, Mo及びCa等が添加されてもよい。

とりわけ、三成分系では、0.10モル%以下のSr, Ba
の添加が圧電特性の改善に一層好ましい。また、三成分
系では、0.10モル%以下のMn, Niの添加が、そ
の焼結性を改善するので好ましい。

【0026】圧電体薄膜15を形成する過程で、既述の
ような構造を得るために、所定の熱処理が行われる。本
発明者らが検討したところによれば、この熱処理の際に
PZT中の酸素が下電極中に拡散する。後述するよう
に、下電極をスパッタリングによって形成すると電極が
PZTと同様に柱状構造を持つことを確認している。こ
の結晶構造では、結晶粒界に酸素がトラップされる傾向
が強く、また、白金内に拡散したチタンがこの結晶粒界
において酸化物を形成する。

【0027】そこで、本発明者は、以下に示すように、
PZTをアニールする前に下電極を酸素存在下で熱処理
を形成することを提案した。図4は、次に述べる方法に
よって形成された圧電体薄膜素子の幅方向の断面を示す

ものであり、加速電圧15kV、引出し電圧4.0kVの条件下で得られた走査型顕微鏡写真である。

【0028】これによれば、下電極及び圧電体膜ともほぼ既述した柱状な結晶構造を持っていることが分かる。下電極中の各結晶粒界に圧電体薄膜中の酸素がトラップされる。また、下電極の酸素雰囲気下での熱処理によって、白金内に拡散した酸素とTiとの化合物が、下電極中で等分散した丸い粒として現われている。

【0029】次に、本発明の一実施形態に係わる圧電体薄膜素子の製造方法について図面を参照して説明する。

【0030】図5(a)ないし図5(c)は、前述した圧電体薄膜素子の製造工程を示す断面図である。図5(a)に示す工程では、シリコン基板11に熱酸化を行い、シリコン基板11上に、膜厚が0.3~1.2μm程度のシリコン酸化膜12を形成する。次に、スパッタ法により、シリコン酸化膜12上に、全体としての膜厚が、0.01μm乃至0.04μm程度のTi/TiO₂/Tiからなるチタン膜13を形成する。次いで、スパッタ法により、チタン膜13上に、プラチナからなる下電極14を、0.2~0.8μm程度の膜厚で形成する。

【0031】この時のスパッタ条件は次のとおりである。装置としては、直流スパッタ装置を用いた。スパッタ圧力条件は、0.4Paである。電圧条件は、Ptの場合には1kwであり、Tiの場合には200wであり、TiO₂の場合には300wである。雰囲気ガスの条件は、PtとTiの場合はアルゴン中であり、TiO₂の場合はO₂/Ar=10/90である。

【0032】次いで、この製膜途中の素子を拡散炉に入れて、酸素雰囲気(酸素分圧60%以上)下、400乃至600℃で30乃至60分間加熱する。又は、RTA(Rapid Thermal Annealing)炉にこの素子を入れ、酸素雰囲気中(流量5L/min)で、温度400乃至600℃で、時間が60乃至300秒加熱する。

【0033】次に、図5(b)に示す工程のように、図5(a)に示す工程で形成した下電極14上に、チタンをスパッタ法により島状に形成する。このチタンを、40乃至60オングストロームの膜厚にすることにより、圧電体薄膜の結晶構造を100面に強く配向させることができる。

【0034】次いで、この上にこのPZT膜15を製膜する。これは例えば、ゾルゲル法によって行う。ここでは、ゾルゲル法を用いてPZTを8回重ね塗りの多層コートによって製造することとする。このゾルゲル法は次のとおりである。

【0035】この製造方法は、PZT膜15を形成可能な金属成分の水酸化物の水和錯体、すなわちゾルを脱水処理してゲルとし、このゲルを加熱焼成して無機酸化物を調整する方法である。この製造方法は次の各工程からなる。

【0036】a. ゾル組成物の成膜工程

本実施の形態において、PZT膜を構成する金属成分のゾルは、PZT膜を形成可能な金属のアルコキシドまたはアセートを、例えば酸で加水分解して調整することができる。本発明においては、ゾル中の金属の組成を制御することで、前述したPZT膜の組成を得ることができる。すなわち、チタン、ジルコニウム、鉛、さらには他の金属成分のそれぞれのアルコキシドまたはアセートを出発原料とする。

【0037】ここでは、最終的にPZT膜(圧電体薄膜)とされるまでに、PZT膜を構成する金属成分の組成がほぼ維持されるという利点がある。すなわち、焼成およびアニール処理中に金属成分、とりわけ鉛成分の蒸発等による変動が極めて少なく、したがって、これらの出発原料における金属成分の組成は、最終的に得られるPZT膜中の金属組成と一致することになる。つまり、ゲルの組成は生成しようとする圧電体膜(本実施の形態ではPZT膜)に応じて決定される。

【0038】また、本実施の形態では、前述した鉛成分が過剰となるPZT膜を得るため、ゾルにおいて鉛成分を化学量論から要求される量よりも20モル%まで好ましくは15モル%まで過剰にすることが好ましい。

【0039】本実施の形態では、このゾルは有機高分子化合物と混合された組成物として用いられるのが好ましい。この有機高分子化合物は、乾燥及び焼成時に薄膜の残留応力を吸収して、この薄膜にクラックが生じることを有効に防止する。具体的には、この有機高分子を含むゲルを用いると、後述するゲル化された薄膜に細孔が生じる。この細孔が、さらに後述するプレアニール及びアニール工程において薄膜の残留応力を吸収するものと考えられる。ここで、好ましく用いられる有機高分子化合物としては、ポリ酢酸ビニル、ヒドロキシプロピルセルロース、ポリエチレングリコール、ポリエチレングリコールモノメチルエーテル、ポリプロピレングリコール、ポリビニルアルコール、ポリアクリル酸、ポリアミド、ポリアミク酸、アセチルセルロース及びその誘導体、ならびにそれらの共重合体が挙げられる。

【0040】なお、本実施の形態では、ポリ酢酸ビニルを添加することで、0.05μm程度の細孔を多数有する多孔質ゲル薄膜を、ヒドロキシプロピルセルロースを添加することで、1μm以下の大きさでかつ広い分布を持った多孔質ゲル薄膜を形成することができる。

【0041】本実施の形態では、ポリエチレングリコールとして、平均分子量285~420程度のものが好適に用いられる。また、ポリプロピレングリコールとしては、平均分子量300~800程度のものが好適に用いられる。

【0042】本実施の形態に係る製造方法では、まず、このゾル組成物をPZT膜15を形成しようとする下電極14(図5(b)参照)上に塗布する。この時の塗布方法は特に限定されず、通常行われている方法、例えば、

スピンコート、ディップコート、ロールコート、バーコート等によって行うことができる。また、フレキソ印刷、スクリーン印刷、オフセット印刷等によって塗布することもできる。

【0043】また、前記塗布により形成される膜の厚さは、それ以降の工程を考慮すると、後述するゲル化工程において形成される多孔質ゲル薄膜の厚さが $0.3\mu\text{m}$ 以下となるように制御することが望ましく、より好ましくは $0.2\mu\text{m}$ 程度とすることがよい。

【0044】次に、塗布されたゾル組成物を自然乾燥、または 200°C 以下の温度で加熱する。ここで、この乾燥（加熱）された膜上に、前記ゾル組成物をさらに塗布して膜厚を厚くすることもできる。この場合は、下地となる膜は、 80°C 以上の温度で乾燥されることが望ましい。

【0045】b. ゾル組成物からなる膜のゲル化工程次に、前述したゾル組成物の成膜工程で得た膜を焼成し、残留有機物を実質的に含まない非晶質の金属酸化物からなる多孔質ゲル薄膜を形成する。

【0046】焼成は、ゾル組成物の膜をゲル化し、かつ膜中から有機物を除去するのに十分な温度で、十分な時間加熱することによって行う。本実施の形態では、焼成温度を $300\sim 450^\circ\text{C}$ にすることが好ましく、 $350\sim 400^\circ\text{C}$ にすることがさらに好ましい。

【0047】焼成時間は、温度及び使用する炉の形式によって変化するが、例えば、脱脂炉を用いた場合には、 $10\sim 120$ 分程度が好ましく、 $15\sim 60$ 分程度とすることがより好ましい。また、ホットプレートを用いた場合には、 $1\sim 60$ 分程度が好ましく、 $5\sim 30$ 分程度とすることがさらに好ましい。

【0048】以上の工程によって、下電極14上に多孔質ゲル薄膜が形成された。

【0049】c. プレアニール工程

次に、前述した工程bで得た多孔質ゲル薄膜を加熱焼成し、この膜を結晶質の金属酸化膜からなる膜に変換する。

【0050】焼成は、多孔質ゲル薄膜を結晶質の金属酸化物からなる膜に変換するために必要な温度で行うが、結晶中にペロブスカイト型結晶が大部分を占めるまで行う必要はなく、ゲル薄膜が均一に結晶化した時点で終了させればよい。本実施の形態では、焼成温度として $400\sim 800^\circ\text{C}$ の範囲が好ましく、 $550\sim 750^\circ\text{C}$ の範囲で焼成することが、より好ましい。焼成時間は、焼成温度及び使用する炉の形式によって変化するが、例えばアニール炉を使用する場合は、 $0.1\sim 5$ 時間程度が好ましく、 $0.5\sim 2$ 時間程度がより好ましい。また、RTA (Rapid Thermal Annealing) 炉を用いた場合、 $0.1\sim 10$ 分程度が好ましく、 $1\sim 5$ 分程度がより好ましい。

【0051】また、本実施の形態では、このプレアニ

ル工程を二段階に分けて実施することができる。具体的には、まず、第一段階として、 $400\sim 600^\circ\text{C}$ の範囲の温度でアニールを行い、次に、第二段階として、 $600\sim 800^\circ\text{C}$ の範囲の温度でアニールを行うことができる。また、さらに好ましくは、第一段階として、 $450\sim 550^\circ\text{C}$ の範囲の温度でアニールを行い、次に、第二段階として、 $600\sim 750^\circ\text{C}$ の範囲の温度でアニールを行うことができる。

【0052】この工程によって、多孔質ゲル薄膜を結晶質の金属酸化膜からなる膜に変換させた。

【0053】d. 繰り返し工程

次に、以後、前述した工程a、bをさらに3回繰り返し、多孔質ゲル薄膜を4層積層した後、工程Cのプレアニール工程により金属酸化膜からなる膜変換する。次いで、島状のチタンをPZT上に既述の方法によって島状に形成し、既述の工程a、bをさらに4回繰り返す。

【0054】この繰り返し工程の結果得られる積層膜の積層数は、最終的なPZT膜15の膜厚を考慮して適宜決定すればよい。ここでは、一層当たり $0.15\mu\text{m}$ であることが良い。なお、後述する次工程（工程e）においてクラック等が発生しない膜厚であることが好ましいことは言うまでもない。

【0055】この繰り返し工程では、先に形成した膜上に新たに多孔質ゲル薄膜を形成し、その後のプレアニールの結果、新たに形成された多孔質ゲル薄膜は、先に形成された膜と実質的に一体化された膜となる。

【0056】ここで、実質的に一体化された膜とは、積層された層間に不連続層がない場合のみならず、本実施の形態に係る最終的に得られるPZT膜15の場合と異なり、積層された層間に不連続層があってもよい。そして、さらに工程a、b及びcを繰り返す場合には、さらに新たな多孔質ゲル薄膜が形成され、その後のプレアニールの結果、この新たな多孔質ゲル薄膜は、前記で得た結晶質の積層膜と実質的に一体化された膜となる。

【0057】e. ペロブスカイト型結晶成長工程

次に、前記工程dで得た膜に、焼成温度 $600\sim 1200^\circ\text{C}$ 、さらに好ましくは $800\sim 1000^\circ\text{C}$ の範囲でアニールを行う。焼成時間は、焼成温度や、使用する炉の形式によって変化するが、例えば、アニール炉を用いた場合、 $0.1\sim 5$ 時間程度が好ましく、 $0.5\sim 2$ 時間程度がより好ましい。また、RTA炉を用いた場合には、 $0.1\sim 10$ 分程度が好ましく、 $0.5\sim 3$ 分程度がより好ましい。

【0058】また、本実施の形態では、このペロブスカイト型結晶成長工程、すなわち、アニールを二段階に分けて実施する。具体的には、第一段階では、 $600\sim 800^\circ\text{C}$ 程度の温度でアニールを行い、第二段階では、 $800\sim 1000^\circ\text{C}$ の温度でアニールを行う。また、さらに好ましくは、第一段階では、 $600\sim 750^\circ\text{C}$ 程度の温度でアニールを行い、第二段階では、 800

～950℃の温度でアニールを行うことができる。

【0059】以上の操作によって、下電極14上に、チタンを核として成長した柱状の多結晶体からなる、膜厚が1.2μmのPZTが形成される。

【0060】次に、下電極形成後圧電体薄膜を形成するに先だって、既述の熱処理を行った場合（本発明法）と、それを行わなかった以外は全て同一条件にした場合（比較法）との圧電特性の比較について示す。

【0061】

	圧電定数 d_{31}	出力係数 g_{31}	誘電率
本発明法	150 (pC/N)	11.2	1500
従来法	120 (pC/N)	9.0	1500

このように、本発明法によれば、いずれも従来法に比較して圧電特性に優れた圧電体薄膜素子を得ることができる。本発明者が、本発明法によって得られた圧電体薄膜素子において、圧電体薄膜中の酸素濃度と下電極近傍10nm付近の圧電体膜中の酸素濃度を比較したところ、下電極近傍の圧電体膜中の酸素濃度が圧電体薄膜中のそれに比較して大きく、前記比(r)が0.95であったことを確認した。また、下電極近傍の圧電体膜中の酸素濃度は、35原子%であった。

【0062】本発明者が鋭意検討したところ、両者の酸素濃度の比(r)は0.9乃至1.2の範囲であることが好ましく、また、下電極近傍中の酸素濃度は、30乃至60原子%の範囲であることが好ましい。これに対して従来法のこれらの特性は、比(r)が0.67程度であって、本発明とは異なりPZT膜中の酸素濃度の低下が顕著に観察された。なお、これらの酸素濃度の測定は、次のようにして行った。

【0063】圧電体薄膜を低角イオンミリング装置にて薄膜断片化し、これをTEM（透過型電子顕微鏡）にて組成分析した。用いた装置、低角イオンミリングはジャソフゾテックアンドハンダレイリッド社製であり、TEMは、フィリップ社製のFEG-CM200TEMである。尚、TEMによるXEDX観察の際の印加電圧は200kVである。

【0064】測定結果は、4点の平均を取ったデータであり次のとおりである。

【0065】

	PZT膜中	下電極近傍
本発明	33.8	35.3
従来	26.4	39.2

（データの単位は原子%である。）

本発明によれば、圧電定数(d_{31})を20～30%、従来のものに比べて向上できる。

【0066】以上により図5(b)の工程を終了し、次に図5(c)に示す工程に移行する。この工程では図5(b)に示す工程で得たPZT膜15上に、スパッタ法によって、膜厚が、0.2～1.0μm程度のアルミニウムからなる上電極16を形成する。

【0067】このようにして、図2に示すような圧電体薄膜素子を得た。なお、得られたPZT膜15には、クラックの発生がなく、また断面には積層による層状の不連続面も存在していないことが確認された。

【0068】図6は、本発明に係る圧電体薄膜素子を振動子として使用したインクジェット式記録ヘッドの一つのインク溜め部分を示す断面図である。

【0069】実施の形態3に係るインクジェット式記録ヘッドは、図6に示すように、インク溜め27が形成されたシリコン基板21と、シリコン基板21上に形成された振動板22と、振動板22上の所望位置に形成された下電極23と、下電極23上であって、インク溜め27に対応した位置に形成された圧電体薄膜24と、圧電体薄膜24上に形成された上電極25と、シリコン基板21の下面に接合された第2の基板26と、を備えて構成されている。

【0070】下電極23は、実施の形態2で説明した下電極と同様の構成を有している。また、圧電体薄膜24は、実施の形態1で説明したPZT膜と同様の構成を有している。

【0071】このインクジェット式記録ヘッドは、図示しないインク流路を介してインク溜め27にインクが供給される。ここで、下電極23と上電極25とを介して、圧電体膜24に電圧を印加すると、圧電体膜24が変形してインク溜め27内のインクに圧力を加える。この圧力によって、インクが図示しないノズルから吐出され、インクジェット記録を行う。

【0072】ここで、このインクジェット式記録ヘッドは、既述の圧電特性に優れた圧電体薄膜素子を振動子として用いているため、大きな圧力でインクを吐出させることができる。

【0073】

【発明の効果】以上説明したように、本発明に係る圧電体薄膜素子の製造方法によれば、圧電体薄膜素子を形成する過程において、圧電体薄膜中の酸素濃度の低下を防ぐことにより、圧電体特性に優れた圧電体薄膜を提供することができる。

【0074】また、本発明によれば、圧電体薄膜中の酸素濃度の低下を防ぐことにより、圧電体特性に優れた圧電体薄膜を提供することができる。

【0075】さらに、本発明によれば、この圧電体薄膜を備えたアクチュエータ、特にインクジェット式記録ヘッドを提供することができる。

【図面の簡単な説明】

【図1】本発明の実施の形態1に係る圧電体薄膜素子の断面図である。

【図2】実施の形態1に係る圧電体薄膜素子を構成するPZT膜の断面を示す走査型電子顕微鏡(SEM)写真である。

【図3】図2に示すPZT膜の平面を示す走査型電子顕

微鏡写真である。

【図4】本発明の製造工程によって得られた圧電体薄膜素子の断面を示す走査型顕微鏡（SEM）写真である。

【図5】(a)ないし(c)は、前述した圧電体薄膜素子の製造工程を示す断面図である。

【図6】本発明に係る圧電体薄膜素子を振動子として使用したインクジェット式記録ヘッドの一つのインク溜め部分を示す断面図である。

【符号の説明】

11、21 シリコン基板

12 シリコン酸化膜

13 チタン酸化膜

14、23 下電極

14B チタン種結晶

15 PZT膜

16、25 上電極

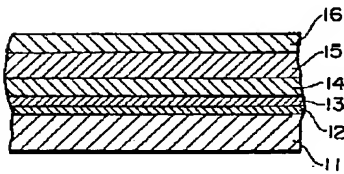
22 振動板

24 圧電体薄膜

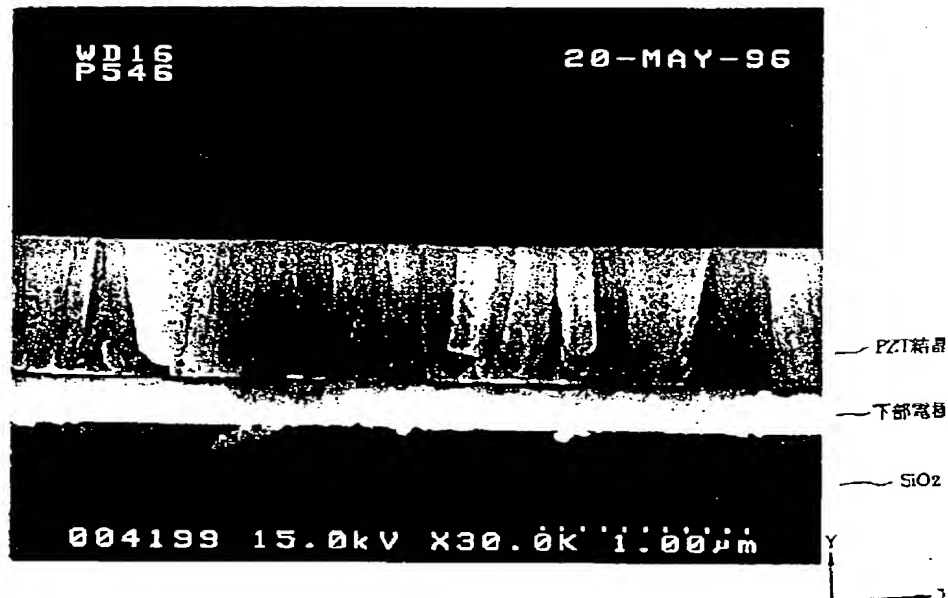
26 基板

10 27 インク溜り

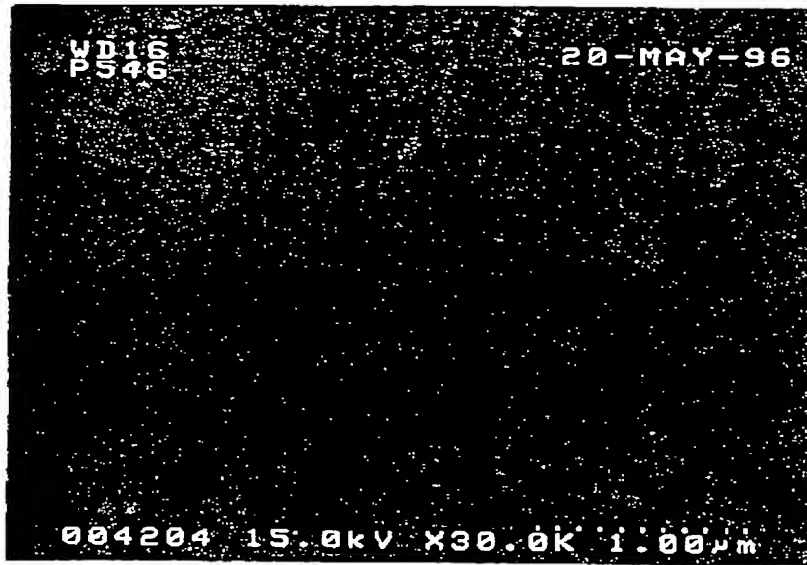
【図1】



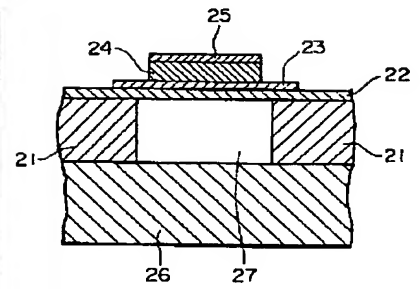
【図2】



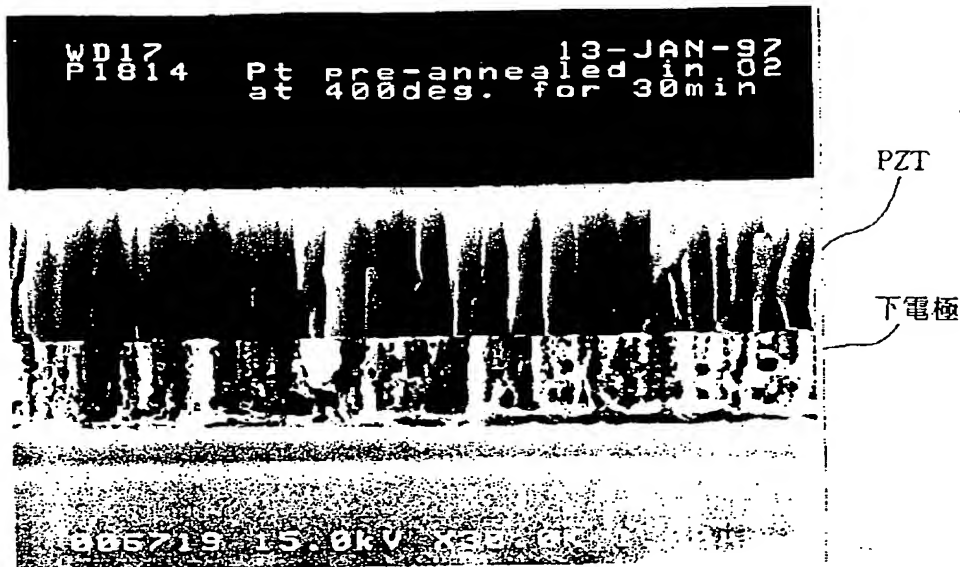
【図3】



【図6】



【図4】



【図5】

